Characterization of Nanoparticles at Environmentally Relevant Concentrations in Aquatic Media by Coupling Asymmetric Flow Field-Flow Fractionation with Single Particle – Inductively Coupled Plasma Mass Spectrometry

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Abstract

An advanced analytical method using asymmetric flow field-flow fractionation (AsFlFFF) and inductively coupled plasma mass spectrophotometry operated in single particle mode (spICP-MS) is developed to detect and quantify silver nanoparticles (AgNPs). Different from previous studies, the AsFlFFF and spICP-MS are directly connected for real-time determination of mass-based and hydrodynamic diameters of nanoparticles. Experimental results show that the AsFlFFF-spICP-MS is capable of detecting and quantifying AgNPs in complex mixtures such as the one containing 40, 60, 80 nm AgNPs and Ag-SiO_2 core-shell nanoparticles

Objectives

- Optimizing the performance of AsFlFFF in separating 40 – 100 nm AgNPs within 30 min: carrier, channel flow, cross flow, focusing time, particle concentrations, and cleaning procedures
- Optimizing spICP-MS measurements: dwell-time and particle concentrations
- Investigate the performance of the AsFlFFF-spICP-MS using mixtures containing different sizes and kinds of AgNPs

Background

- AgNPs are the most commonly used engineered nanomaterials in consumer products → AgNPs are likely to end up in the environment and possibly cause adverse impacts on ecosystem and human health
- To study the fate and transport, and assess the risk of AgNPs, it is critical to detect and quantify AgNPs in environmental samples
- Currently, methods used to detect, quantify, and characterize of AgNPs are not well developed

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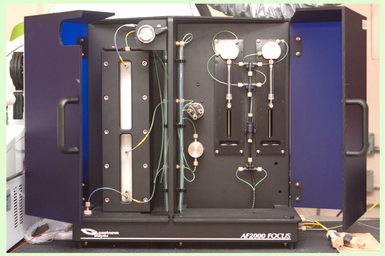
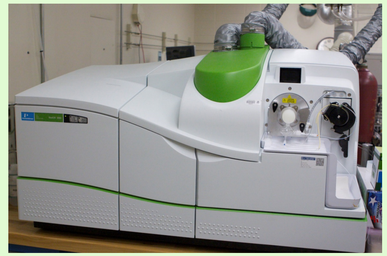
store.sealshield.com/silver-seal-keyboard-p26.aspx

- AsFlFFF (combining with ICP-MS) and spICP-MS alone cannot provide detailed AgNP information such as coating layer thickness and aggregation state
- By using AsFlFFF-spICP-MS, the coating layer thickness and aggregation state of AgNPs can be determined since AsFlFFF-spICP-MS is able to measure both hydrodynamic diameter and mass-based diameter of detected AgNPs simultaneously.

Coupling AsFlFFF with sp-ICP-MS





The channel flow from the AsFlFFF directly entered the ICP-MS

AF2000 Focus (Postnova Analytic)

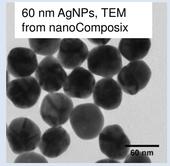
Carrier	0.02 % FL-70
Membrane	10 kDa RC
Channel thickness	350 µm
Channel flow	1.5 mL/min
Cross flow	1.2 mL/min
Focusing time	3 min

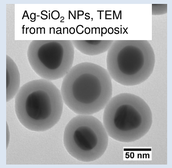
NexION 300D (PerkinElmer) with Nano Application for Syngistix ICPMS Software

Flow rate	1.5 mL/min
Dwell-time	5 ms
Sampling time	30 min
Data acquisition	after focusing

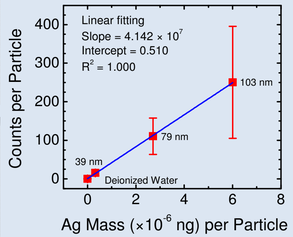
Nanoparticles

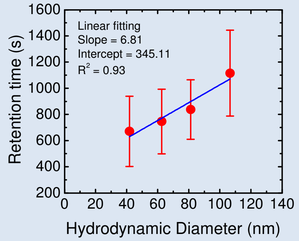
- 60 nm AuNPs (NIST 8013)
- 40, 60, 80, and 100 nm AgNPs (nanoComposix)
- Ag-SiO_2 core-shell nanoparticles (nanoComposix, total diameter = 92.3 nm, Ag core diameter = 51.0 nm) – modeled (i) AgNPs with coating layer or (ii) AgNP heteroaggregates





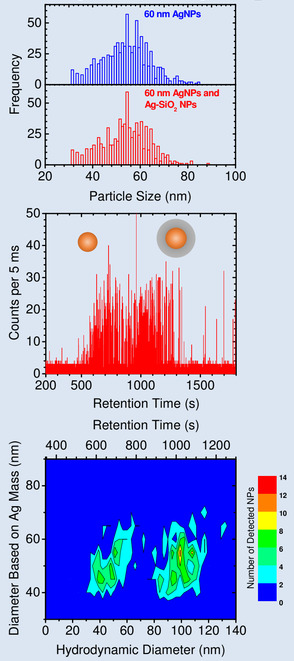
Calibration curves used in AsFlFFF-spICP-MS



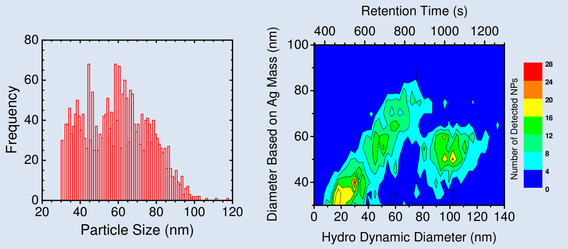


AsFlFFF-spICP-MS Results

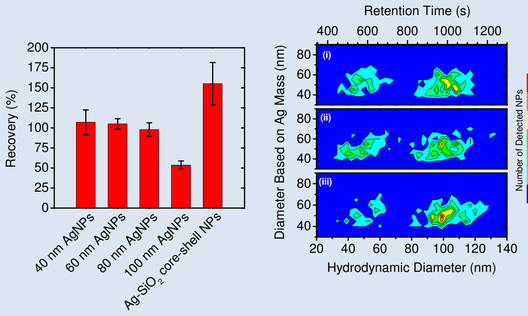
- 60 nm AgNPs and Ag-SiO_2 NPs



- 40 – 80 nm AgNPs and Ag-SiO_2 NPs



- Recovery and Reproducibility



Conclusions. AsFlFFF-spICP-MS successfully (i) differentiates 60 nm AgNPs from Ag-SiO_2 core-shell NPs and (ii) detects and quantifies AgNPs in a complex mixture containing 40 – 60 nm AgNPs and Ag-SiO_2 core-shell NPs. The recovery and reproducibility of this technique are good to moderate depending on particle size and type.

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